Arene C–H Bond Activation and Arene Oxidative Coupling by Cationic Palladium(II) Complexes.

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Supporting Information Available: Summary of C–H bond activation kinetic data and derivation of the rate law for Scheme 3. In all cases, [Pd] is kept at 0.01 – 0.011 *M*; the observed rate constants have an uncertainty between 5 - 10% of the reported values. Details of the structure determination, tables of atomic coordinates, complete bond distances and angles and anisotropic displacement parameters for complex **5b** (20 pages).

Table S1. Water Concentration Dependence

Pd Complex	Substrate	T (°C)	[substrate](*M*)	[D_2O] (*M*)	k_{obs} (x 10^4)
2a	C_6H_6	25	0.218	0.056	33.2
2a	C_6H_6	25	0.218	0.056	32.3
2a	C_6H_6	25	0.218	0.133	30.2
2a	C_6H_6	25	0.218	0.133	33.3
2a	C_6H_6	25	0.218	0.133	29.4
2a	C_6H_6	25	0.218	0.249	16.7
2a	C_6H_6	25	0.218	0.249	22.6
2a	C_6H_6	25	0.218	0.442	12.5
2a	C_6H_6	25	0.218	0.442	13.9
2a	C_6D_6	25	0.220	0.442	3.2
2a	C_6H_6	25	0.218	0.828	9.6
2a	C_6H_6	25	0.218	0.828	10.2
2a	C_6H_6	25	0.218	1.21	7.3
2a	C_6H_6	25	0.218	2.37	4.6
2a	C_6H_6	25	0.218	4.68	2.7
2b	C_6H_6	25	0.222	0.215	15.0
2b	C_6H_6	25	0.222	0.215	14.5
2b	C_6H_6	25	0.222	0.450	7.4
2b	C_6H_6	25	0.233	0.474	7.3
2b	C_6H_6	25	0.220	0.747	5.2
2b	C_6H_6	25	0.220	0.747	5.3

Table S2. Ionic Strength Experiments

Pt Complex	Substrate	T (°C)	Substrate (*M*)	$[D_2O]$ (*M*)	NMe_4BF_4 (*M*)	k_{obs} (x 10^4)
2a	C_6H_6	25	0.218	0.442	--	13.1
2a	C_6H_6	25	0.218	0.442	0.10	13.0
2a	C_6H_6	25	0.218	0.828	--	10.2
2a	C_6H_6	25	0.218	0.828	0.10	9.6

Table S3. Temperature Dependence

Pt Complex	Substrate	T (°C)	[substrate](*M*)	$[D_2O]$ (*M*)	k_{obs} (x 10^4)
2a	C_6H_6	1.1	0.218	0.442	0.43
2a	C_6H_6	25	0.218	0.442	13.1
2a	C_6H_6	41	0.218	0.442	53.9

Table S4. $[C_6H_6]$ Dependence

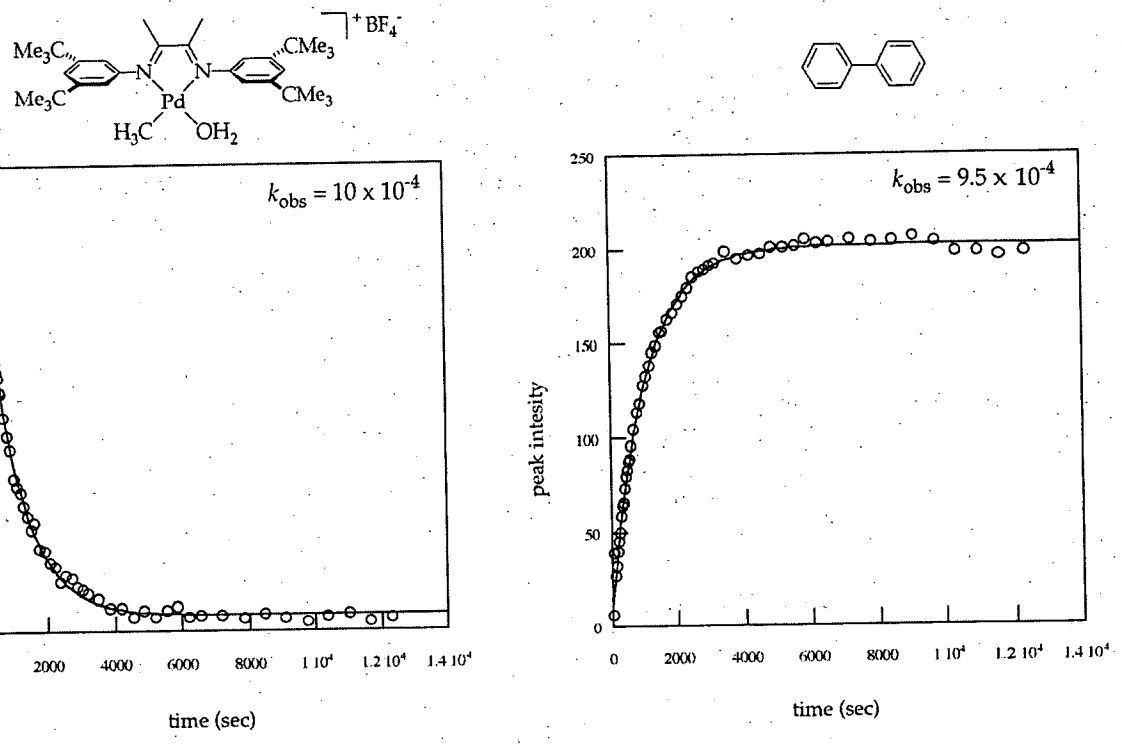
Pt Complex	Substrate	T (°C)	[substrate](*M*)	$[D_2O]$ (*M*)	k_{obs} (x 10^4)
2a	C_6H_6	25	0.109	0.442	7.1
2a	C_6H_6	25	0.218	0.442	13.1
2a	C_6H_6	25	0.435	0.442	24.7
2b	C_6H_6	25	0.111	0.451	2.5
2b	C_6H_6	25	0.233	0.451	7.4
2b	C_6H_6	25	0.435	0.451	13.3

Table S5. Substrate Dependence

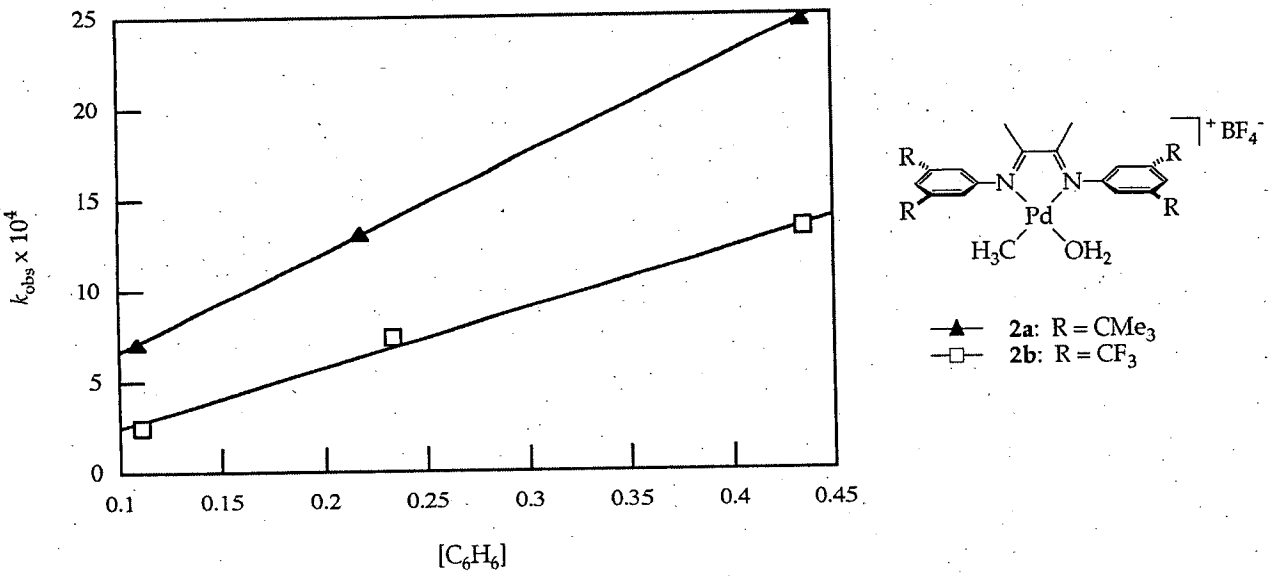
Pt Complex	Substrate	T (°C)	[substrate](*M*)	$[D_2O]$ (*M*)	k_{obs} (x 10^4)
2a	C_6H_6	25	0.218	0.442	13.1
2a	$C_6H_5CH_3$	25	0.217	0.442	26.8
2a	$C_6H_5CF_3$	25	0.220	0.449	1.1

Kinetic Plots:

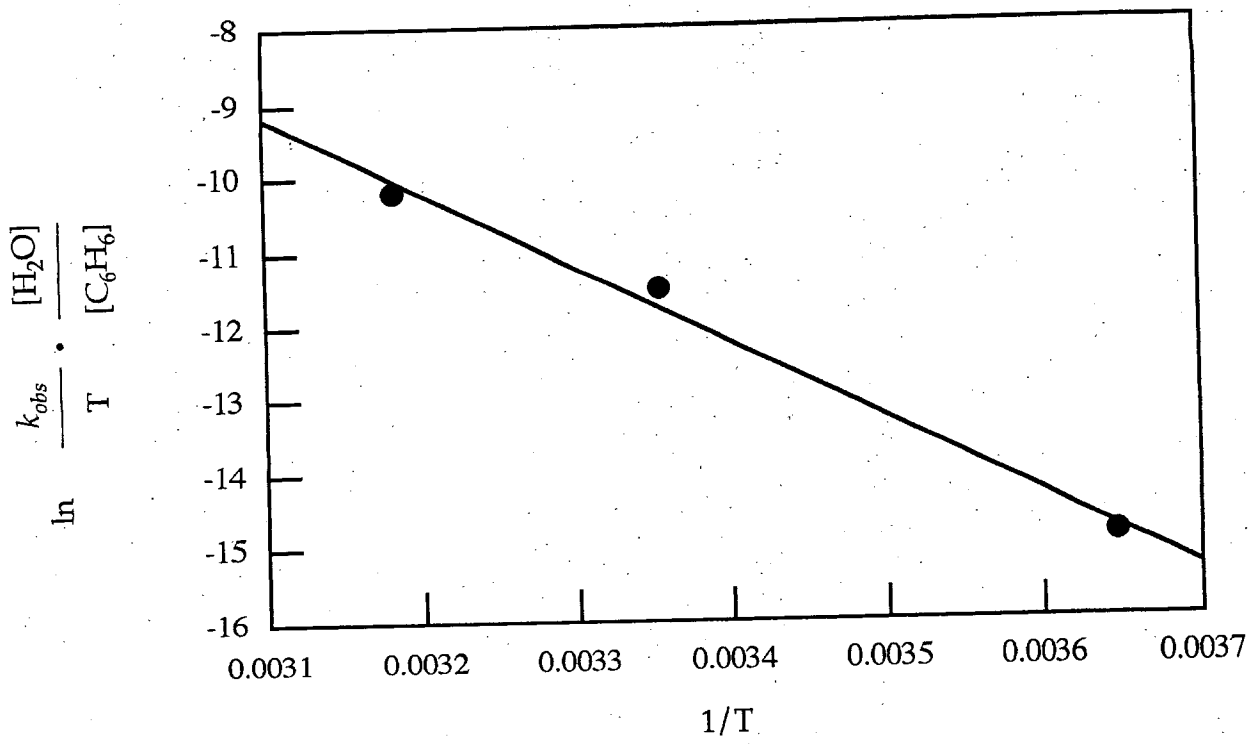
Plot 1. Representative exponential fits for decay of starting material and appearance of product (biphenyl) for the reaction of **2a** with benzene.



Plot 2. Benzene concentration dependence.



Plot 3. Eyring plot.



Rate Law Derivation

$$\text{Define } [Pd]_T = [\mathbf{A}i] + [\mathbf{A}ii] \qquad K_{eq} = \frac{[\mathbf{A}ii][TFE]}{[\mathbf{A}i][H_2O]}$$

$$\text{Then } [Pd]_T = [\mathbf{A}i]\left[1 + \frac{K_{eq}[H_2O]}{[TFE]}\right]; \quad [\mathbf{A}i] = \frac{[Pd]_T}{1 + \frac{K_{eq}[H_2O]}{[TFE]}}$$

$$-\frac{d[Pd]_T}{dt} = k_2[\mathbf{B}]$$

Applying the steady-state approximation on [**B**]

$$\frac{d[\mathbf{B}]}{dt} = k_1[\mathbf{A}i][C_6H_6] - k_{-1}[\mathbf{B}][TFE] - k_2[\mathbf{B}] \cong 0$$

$$[\mathbf{B}] = \frac{k_1[\mathbf{A}i][C_6H_6]}{k_{-1}[TFE] + k_2}$$

$$-\frac{d[Pd]_T}{dt} = k_2 \cdot \frac{k_1[C_6H_6]}{k_{-1}[TFE] + k_2} \cdot \frac{[Pd]_T}{1 + \frac{K_{eq}[H_2O]}{[TFE]}}$$

$$= k_{obs}[Pd]_T = \frac{k_2}{k_{-1}[TFE] + k_2} \cdot \frac{k_1[TFE][C_6H_6][Pd]_T}{[TFE] + K_{eq}[H_2O]}$$

Expression for $1/k_{obs}$ vs. $[H_2O]/[C_6H_6]$ plot:

$$\frac{1}{k_{obs}} = \frac{k_{-1}[TFE] + k_2}{k_2} \cdot \frac{[TFE] + K_{eq}[H_2O]}{k_1[TFE][C_6H_6]}$$

$$= \underbrace{\frac{k_{-1}[TFE] + k_2}{k_2} \cdot \frac{K_{eq}[H_2O]}{k_1[TFE][C_6H_6]}} + \underbrace{\frac{k_{-1}[TFE] + k_2}{k_2} \cdot \frac{[TFE]}{k_1[TFE][C_6H_6]}}$$

$$\text{slope} = \frac{k_{-1}[TFE] + k_2}{k_2} \cdot \frac{K_{eq}}{k_1[TFE]} \qquad \text{intercept} = \frac{k_{-1}[TFE] + k_2}{k_2} \cdot \frac{1}{k_1[C_6H_6]}$$

$$\frac{\text{intercept}}{\text{slope}} = \frac{1}{k_1[C_6H_6]} \cdot \frac{k_1[TFE]}{K_{eq}} = \frac{[TFE]}{K_{eq}[C_6H_6]}$$

K_{eq} calculated indirectly by this method

Table S6. Crystal data and structure refinement for 5b (CCDC 204983).

Empirical formula	$C_{40}H_{24}B_2F_{32}N_4O_2Pd_2$
Formula weight	1435.05
Crystallization Solvent	Trifluoroethanol
Crystal Habit	Plate
Crystal size	0.26 x 0.14 x 0.09 mm^3
Crystal color	Yellow

Data Collection

Preliminary Photos	Rotation
Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKα
Data Collection Temperature	98(2) K
θ range for 30482 reflections used in lattice determination	2.19 to 28.43°
Unit cell dimensions	a = 15.7429(7) Å b = 10.3772(5) Å β= 108.1380(10)° c = 15.8713(7) Å
Volume	2464.01(19) $Å^3$
Z	2
Crystal system	Monoclinic
Space group	$P2_1$
Density (calculated)	1.934 Mg/m^3
F(000)	1396
Data collection program	Bruker SMART v5.054
θ range for data collection	1.59 to 28.44°
Completeness to θ = 28.44°	94.4 %
Index ranges	$-20 \le h \le 20, -13 \le k \le 13, -21 \le l \le 20$
Data collection scan type	ω scans at 7 ϕ settings
Data reduction program	Bruker SAINT v6.022
Reflections collected	50764
Independent reflections	11439 [R_{int}= 0.0488]
Absorption coefficient	0.893 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.9280 and 0.8010

Table S6 (cont.)

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	11439 / 1 / 743
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	1.983
Final R indices [I>2σ(I), 10548 reflections]	R1 = 0.0352, *w*R2 = 0.0679
R indices (all data)	R1 = 0.0403, *w*R2 = 0.0686
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.001
Average shift/error	0.000
Absolute structure parameter	0.083(16)
Largest diff. peak and hole	1.004 and -0.683 e.Å^{-3}

Special Refinement Details

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\_(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

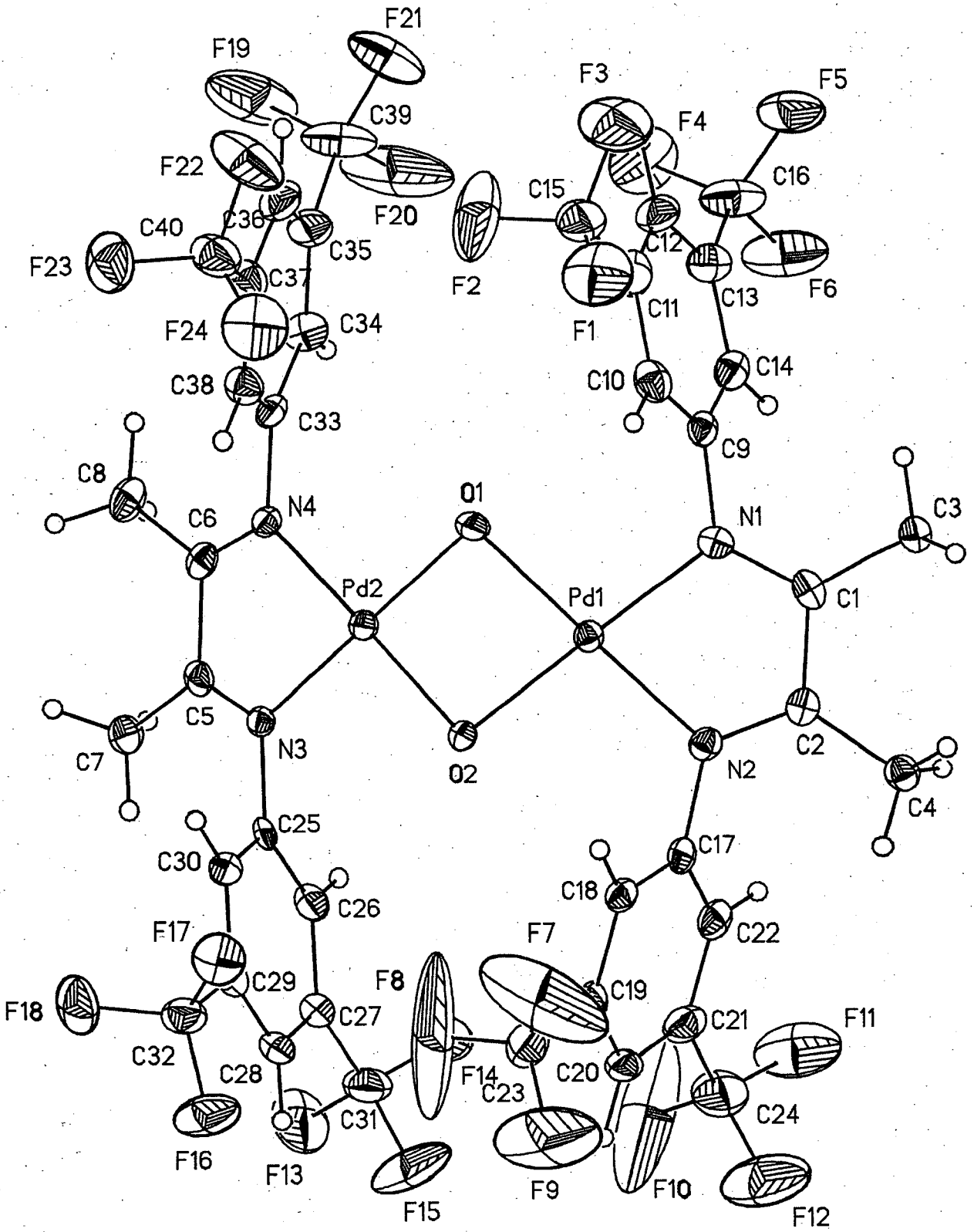


Table S7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 5b (CCDC 204983). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Pd(1)	4929(1)	-17(1)	8366(1)	15(1)
Pd(2)	4903(1)	2021(1)	7044(1)	14(1)
F(1)	1923(2)	-2831(4)	6365(2)	63(1)
F(2)	1467(3)	-1023(4)	5768(2)	83(1)
F(3)	654(2)	-2157(4)	6334(2)	69(1)
F(4)	899(2)	2235(3)	8270(3)	77(1)
F(5)	454(2)	655(3)	8878(2)	53(1)
F(6)	1625(2)	1683(3)	9605(2)	62(1)
F(7)	8021(3)	-2534(6)	8121(4)	159(3)
F(8)	8360(6)	-813(6)	7863(4)	232(5)
F(9)	9188(3)	-1890(6)	8800(3)	135(2)
F(10)	8920(6)	2061(6)	11045(3)	225(5)
F(11)	8309(2)	1159(4)	11869(2)	73(1)
F(12)	9433(2)	386(5)	11688(2)	91(2)
F(13)	9076(2)	4949(4)	8997(2)	69(1)
F(14)	8319(2)	3942(4)	9683(2)	52(1)
F(15)	9441(2)	3044(4)	9437(2)	71(1)
F(16)	9105(2)	872(3)	6687(2)	50(1)
F(17)	7787(2)	146(3)	6066(2)	37(1)
F(18)	8212(2)	1824(3)	5554(2)	44(1)
F(19)	507(2)	4810(4)	5501(3)	91(1)
F(20)	1065(2)	4259(5)	6820(3)	118(2)
F(21)	134(2)	3013(3)	5937(2)	61(1)
F(22)	1080(2)	200(4)	3983(2)	63(1)
F(23)	1973(2)	1211(3)	3422(2)	49(1)
F(24)	2472(2)	-270(3)	4369(2)	57(1)
O(1)	4032(2)	742(3)	7272(2)	19(1)
O(2)	5805(2)	779(3)	7817(2)	17(1)
N(1)	4094(2)	-747(3)	8962(2)	17(1)
N(2)	5792(2)	-749(3)	9467(2)	17(1)
N(3)	5741(2)	3380(3)	6908(2)	14(1)
N(4)	4050(2)	3337(3)	6348(2)	16(1)
C(1)	4457(3)	-1308(3)	9719(3)	17(1)
C(2)	5446(3)	-1328(4)	10003(3)	17(1)
C(3)	3949(3)	-1915(4)	10267(3)	20(1)
C(4)	5965(3)	-1995(4)	10837(3)	21(1)
C(5)	5385(3)	4475(4)	6617(2)	18(1)
C(6)	4390(3)	4448(4)	6283(2)	18(1)
C(7)	5873(3)	5675(4)	6565(3)	22(1)
C(8)	3888(3)	5614(4)	5859(3)	25(1)
C(9)	3142(3)	-622(4)	8551(3)	17(1)
C(10)	2775(3)	-1246(4)	7742(3)	25(1)
C(11)	1879(3)	-1077(5)	7308(3)	32(1)
C(12)	1362(3)	-300(5)	7638(3)	32(1)
C(13)	1744(3)	344(4)	8469(3)	26(1)
C(14)	2638(3)	151(4)	8918(3)	21(1)
C(15)	1468(3)	-1785(6)	6432(3)	44(1)

C(16)	1185(3)	1222(5)	8806(4)	44(1)
C(17)	6738(3)	-617(4)	9624(3)	19(1)
C(18)	7100(3)	-1124(4)	9014(3)	20(1)
C(19)	8002(3)	-955(4)	9129(3)	27(1)
C(20)	8521(3)	-257(4)	9849(3)	28(1)
C(21)	8142(3)	242(4)	10452(3)	29(1)
C(22)	7252(3)	73(4)	10352(2)	22(1)
C(23)	8396(4)	-1499(6)	8474(3)	37(1)
C(24)	8704(4)	1018(6)	11245(4)	46(1)
C(25)	6682(2)	3135(4)	7178(3)	18(1)
C(26)	7236(3)	3618(4)	7964(3)	22(1)
C(27)	8138(3)	3285(4)	8211(3)	24(1)
C(28)	8482(3)	2510(4)	7693(3)	25(1)
C(29)	7909(2)	2048(5)	6909(3)	22(1)
C(30)	7004(2)	2337(4)	6647(3)	19(1)
C(31)	8748(3)	3805(5)	9070(3)	34(1)
C(32)	8263(3)	1224(5)	6311(3)	30(1)
C(33)	3126(3)	3022(4)	5947(2)	18(1)
C(34)	2450(3)	3563(4)	6211(3)	24(1)
C(35)	1578(3)	3182(5)	5802(3)	30(1)
C(36)	1373(3)	2249(5)	5125(3)	30(1)
C(37)	2055(3)	1719(4)	4883(3)	26(1)
C(38)	2939(2)	2085(5)	5292(2)	23(1)
C(39)	825(3)	3788(6)	6027(4)	52(2)
C(40)	1875(3)	710(6)	4158(3)	39(1)
B(1)	4985(4)	9006(5)	5854(4)	35(1)
F(25)	4214(2)	8805(3)	6108(2)	40(1)
F(26)	5723(2)	8854(2)	6591(2)	36(1)
F(27)	4970(2)	10286(2)	5556(2)	42(1)
F(28)	4973(2)	8176(3)	5180(2)	43(1)
B(2)	5051(4)	6127(5)	8543(3)	26(1)
F(29)	5989(2)	6138(3)	9035(2)	67(1)
F(30)	4624(2)	6152(3)	9168(2)	57(1)
F(31)	4896(2)	4951(3)	8097(1)	31(1)
F(32)	4869(2)	7140(3)	7993(2)	35(1)

Table S8. Selected bond lengths [Å] and angles [°] for 5b (CCDC 204983).

Pd(1)-N(1)	1.993(3)	N(1)-Pd(1)-Pd(2)	137.71(9)
Pd(1)-N(2)	2.000(3)	N(2)-Pd(1)-Pd(2)	138.07(9)
Pd(1)-O(2)	2.022(3)	O(2)-Pd(1)-Pd(2)	42.80(7)
Pd(1)-O(1)	2.025(3)	O(1)-Pd(1)-Pd(2)	42.74(7)
Pd(1)-Pd(2)	2.9706(4)	N(3)-Pd(2)-N(4)	79.00(12)
Pd(2)-N(3)	1.987(3)	N(3)-Pd(2)-O(1)	174.61(12)
Pd(2)-N(4)	1.991(3)	N(4)-Pd(2)-O(1)	99.85(12)
Pd(2)-O(1)	2.022(3)	N(3)-Pd(2)-O(2)	98.86(11)
Pd(2)-O(2)	2.025(2)	N(4)-Pd(2)-O(2)	175.98(13)
		O(1)-Pd(2)-O(2)	81.96(10)
N(1)-Pd(1)-N(2)	79.03(13)	N(3)-Pd(2)-Pd(1)	135.89(9)
N(1)-Pd(1)-O(2)	177.05(12)	N(4)-Pd(2)-Pd(1)	137.59(9)
N(2)-Pd(1)-O(2)	99.37(12)	O(1)-Pd(2)-Pd(1)	42.82(7)
N(1)-Pd(1)-O(1)	99.60(12)	O(2)-Pd(2)-Pd(1)	42.74(7)
N(2)-Pd(1)-O(1)	178.24(12)	Pd(2)-O(1)-Pd(1)	94.44(11)
O(2)-Pd(1)-O(1)	81.94(10)	d(1)-O(2)-Pd(2)	94.45(11)

Symmetry transformations used to generate equivalent atoms:

Table S9. Bond lengths [Å] and angles [°] for 5b (CCDC 204983).

Pd(1)-N(1)	1.993(3)	C(5)-C(6)	1.489(6)
Pd(1)-N(2)	2.000(3)	C(6)-C(8)	1.487(5)
Pd(1)-O(2)	2.022(3)	C(7)-H(7A)	0.9800
Pd(1)-O(1)	2.025(3)	C(7)-H(7B)	0.9800
Pd(1)-Pd(2)	2.9706(4)	C(7)-H(7C)	0.9800
Pd(2)-N(3)	1.987(3)	C(8)-H(8A)	0.9800
Pd(2)-N(4)	1.991(3)	C(8)-H(8B)	0.9800
Pd(2)-O(1)	2.022(3)	C(8)-H(8C)	0.9800
Pd(2)-O(2)	2.025(2)	C(9)-C(14)	1.378(5)
F(1)-C(15)	1.323(7)	C(9)-C(10)	1.393(5)
F(2)-C(15)	1.318(6)	C(10)-C(11)	1.375(6)
F(3)-C(15)	1.300(5)	C(10)-H(10)	0.9500
F(4)-C(16)	1.339(6)	C(11)-C(12)	1.361(7)
F(5)-C(16)	1.329(6)	C(11)-C(15)	1.527(7)
F(6)-C(16)	1.330(6)	C(12)-C(13)	1.433(6)
F(7)-C(23)	1.268(7)	C(12)-H(12)	0.9500
F(8)-C(23)	1.190(6)	C(13)-C(14)	1.379(6)
F(9)-C(23)	1.259(6)	C(13)-C(16)	1.478(7)
F(10)-C(24)	1.206(7)	C(14)-H(14)	0.9500
F(11)-C(24)	1.330(7)	C(17)-C(18)	1.371(5)
F(12)-C(24)	1.319(6)	C(17)-C(22)	1.386(6)
F(13)-C(31)	1.314(6)	C(18)-C(19)	1.386(6)
F(14)-C(31)	1.353(5)	C(18)-H(18)	0.9500
F(15)-C(31)	1.326(5)	C(19)-C(20)	1.384(7)
F(16)-C(32)	1.325(5)	C(19)-C(23)	1.479(6)
F(17)-C(32)	1.335(5)	C(20)-C(21)	1.376(6)
F(18)-C(32)	1.333(5)	C(20)-H(20)	0.9500
F(19)-C(39)	1.346(7)	C(21)-C(22)	1.372(6)
F(20)-C(39)	1.292(7)	C(21)-C(24)	1.523(7)
F(21)-C(39)	1.324(6)	C(22)-H(22)	0.9500
F(22)-C(40)	1.307(5)	C(25)-C(26)	1.376(5)
F(23)-C(40)	1.331(6)	C(25)-C(30)	1.384(5)
F(24)-C(40)	1.354(6)	C(26)-C(27)	1.393(6)
N(1)-C(1)	1.297(5)	C(26)-H(26)	0.9500
N(1)-C(9)	1.443(5)	C(27)-C(28)	1.377(6)
N(2)-C(2)	1.292(5)	C(27)-C(31)	1.502(6)
N(2)-C(17)	1.438(5)	C(28)-C(29)	1.376(6)
N(3)-C(5)	1.287(5)	C(28)-H(28)	0.9500
N(3)-C(25)	1.431(5)	C(29)-C(30)	1.387(5)
N(4)-C(6)	1.289(5)	C(29)-C(32)	1.508(6)
N(4)-C(33)	1.432(5)	C(30)-H(30)	0.9500
C(1)-C(2)	1.480(5)	C(33)-C(34)	1.379(6)
C(1)-C(3)	1.492(5)	C(33)-C(38)	1.386(6)
C(2)-C(4)	1.492(5)	C(34)-C(35)	1.381(6)
C(3)-H(3A)	0.9800	C(34)-H(34)	0.9500
C(3)-H(3B)	0.9800	C(35)-C(36)	1.408(7)
C(3)-H(3C)	0.9800	C(35)-C(39)	1.480(7)
C(4)-H(4A)	0.9800	C(36)-C(37)	1.364(6)
C(4)-H(4B)	0.9800	C(36)-H(36)	0.9500
C(4)-H(4C)	0.9800	C(37)-C(38)	1.392(5)
C(5)-C(7)	1.480(5)	C(37)-C(40)	1.515(6)

C(38)-H(38)	0.9500
B(1)-F(28)	1.369(6)
B(1)-F(26)	1.378(6)
B(1)-F(27)	1.407(6)
B(1)-F(25)	1.409(7)
B(2)-F(32)	1.338(6)
B(2)-F(30)	1.361(5)
B(2)-F(31)	1.394(5)
B(2)-F(29)	1.439(6)
N(1)-Pd(1)-N(2)	79.03(13)
N(1)-Pd(1)-O(2)	177.05(12)
N(2)-Pd(1)-O(2)	99.37(12)
N(1)-Pd(1)-O(1)	99.60(12)
N(2)-Pd(1)-O(1)	178.24(12)
O(2)-Pd(1)-O(1)	81.94(10)
N(1)-Pd(1)-Pd(2)	137.71(9)
N(2)-Pd(1)-Pd(2)	138.07(9)
O(2)-Pd(1)-Pd(2)	42.80(7)
O(1)-Pd(1)-Pd(2)	42.74(7)
N(3)-Pd(2)-N(4)	79.00(12)
N(3)-Pd(2)-O(1)	174.61(12)
N(4)-Pd(2)-O(1)	99.85(12)
N(3)-Pd(2)-O(2)	98.86(11)
N(4)-Pd(2)-O(2)	175.98(13)
O(1)-Pd(2)-O(2)	81.96(10)
N(3)-Pd(2)-Pd(1)	135.89(9)
N(4)-Pd(2)-Pd(1)	137.59(9)
O(1)-Pd(2)-Pd(1)	42.82(7)
O(2)-Pd(2)-Pd(1)	42.74(7)
Pd(2)-O(1)-Pd(1)	94.44(11)
Pd(1)-O(2)-Pd(2)	94.45(11)
C(1)-N(1)-C(9)	123.7(3)
C(1)-N(1)-Pd(1)	116.4(3)
C(9)-N(1)-Pd(1)	119.8(2)
C(2)-N(2)-C(17)	123.9(3)
C(2)-N(2)-Pd(1)	116.1(3)
C(17)-N(2)-Pd(1)	120.0(2)
C(5)-N(3)-C(25)	124.0(3)
C(5)-N(3)-Pd(2)	115.8(3)
C(25)-N(3)-Pd(2)	120.1(2)
C(6)-N(4)-C(33)	124.0(3)
C(6)-N(4)-Pd(2)	115.6(3)
C(33)-N(4)-Pd(2)	120.4(2)
N(1)-C(1)-C(2)	114.0(3)
N(1)-C(1)-C(3)	124.6(4)
C(2)-C(1)-C(3)	121.4(3)
N(2)-C(2)-C(1)	114.4(3)
N(2)-C(2)-C(4)	124.9(4)
C(1)-C(2)-C(4)	120.7(3)
C(1)-C(3)-H(3A)	109.5
C(1)-C(3)-H(3B)	109.5
H(3A)-C(3)-H(3B)	109.5
C(1)-C(3)-H(3C)	109.5
H(3A)-C(3)-H(3C)	109.5
H(3B)-C(3)-H(3C)	109.5
C(2)-C(4)-H(4A)	109.5
C(2)-C(4)-H(4B)	109.5
H(4A)-C(4)-H(4B)	109.5
C(2)-C(4)-H(4C)	109.5
H(4A)-C(4)-H(4C)	109.5
H(4B)-C(4)-H(4C)	109.5
N(3)-C(5)-C(7)	126.0(4)
N(3)-C(5)-C(6)	113.8(3)
C(7)-C(5)-C(6)	120.2(3)
N(4)-C(6)-C(8)	126.0(4)
N(4)-C(6)-C(5)	113.9(3)
C(8)-C(6)-C(5)	119.9(3)
C(5)-C(7)-H(7A)	109.5
C(5)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(5)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(6)-C(8)-H(8A)	109.5
C(6)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(6)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(14)-C(9)-C(10)	122.2(4)
C(14)-C(9)-N(1)	121.0(3)
C(10)-C(9)-N(1)	116.7(4)
C(11)-C(10)-C(9)	118.0(4)
C(11)-C(10)-H(10)	121.0
C(9)-C(10)-H(10)	121.0
C(12)-C(11)-C(10)	121.7(4)
C(12)-C(11)-C(15)	120.0(4)
C(10)-C(11)-C(15)	118.2(5)
C(11)-C(12)-C(13)	120.0(4)
C(11)-C(12)-H(12)	120.0
C(13)-C(12)-H(12)	120.0
C(14)-C(13)-C(12)	118.4(4)
C(14)-C(13)-C(16)	122.0(4)
C(12)-C(13)-C(16)	119.6(4)
C(9)-C(14)-C(13)	119.6(4)
C(9)-C(14)-H(14)	120.2
C(13)-C(14)-H(14)	120.2
F(3)-C(15)-F(2)	109.1(4)
F(3)-C(15)-F(1)	106.6(5)
F(2)-C(15)-F(1)	107.1(5)
F(3)-C(15)-C(11)	112.1(4)
F(2)-C(15)-C(11)	109.5(5)
F(1)-C(15)-C(11)	112.4(4)
F(5)-C(16)-F(6)	106.6(5)
F(5)-C(16)-F(4)	105.8(4)
F(6)-C(16)-F(4)	107.2(4)
F(5)-C(16)-C(13)	112.8(4)

F(6)-C(16)-C(13)	111.9(4)	F(15)-C(31)-F(14)	105.9(4)
F(4)-C(16)-C(13)	112.0(5)	F(13)-C(31)-C(27)	113.8(4)
C(18)-C(17)-C(22)	121.6(4)	F(15)-C(31)-C(27)	113.0(4)
C(18)-C(17)-N(2)	118.5(4)	F(14)-C(31)-C(27)	111.6(4)
C(22)-C(17)-N(2)	119.8(4)	F(16)-C(32)-F(18)	107.8(4)
C(17)-C(18)-C(19)	119.5(4)	F(16)-C(32)-F(17)	107.1(4)
C(17)-C(18)-H(18)	120.2	F(18)-C(32)-F(17)	105.0(4)
C(19)-C(18)-H(18)	120.2	F(16)-C(32)-C(29)	112.8(4)
C(20)-C(19)-C(18)	119.5(4)	F(18)-C(32)-C(29)	111.8(4)
C(20)-C(19)-C(23)	120.8(4)	F(17)-C(32)-C(29)	112.0(4)
C(18)-C(19)-C(23)	119.7(4)	C(34)-C(33)-C(38)	120.6(4)
C(21)-C(20)-C(19)	119.9(4)	C(34)-C(33)-N(4)	123.0(4)
C(21)-C(20)-H(20)	120.0	C(38)-C(33)-N(4)	116.3(3)
C(19)-C(20)-H(20)	120.0	C(33)-C(34)-C(35)	119.3(4)
C(22)-C(21)-C(20)	121.3(4)	C(33)-C(34)-H(34)	120.4
C(22)-C(21)-C(24)	118.2(4)	C(35)-C(34)-H(34)	120.4
C(20)-C(21)-C(24)	120.5(4)	C(34)-C(35)-C(36)	120.9(4)
C(21)-C(22)-C(17)	118.2(4)	C(34)-C(35)-C(39)	121.2(4)
C(21)-C(22)-H(22)	120.9	C(36)-C(35)-C(39)	117.7(4)
C(17)-C(22)-H(22)	120.9	C(37)-C(36)-C(35)	118.6(4)
F(8)-C(23)-F(9)	108.5(6)	C(37)-C(36)-H(36)	120.7
F(8)-C(23)-F(7)	104.4(7)	C(35)-C(36)-H(36)	120.7
F(9)-C(23)-F(7)	100.0(5)	C(36)-C(37)-C(38)	121.2(4)
F(8)-C(23)-C(19)	114.9(5)	C(36)-C(37)-C(40)	121.0(4)
F(9)-C(23)-C(19)	114.4(5)	C(38)-C(37)-C(40)	117.8(4)
F(7)-C(23)-C(19)	113.2(5)	C(33)-C(38)-C(37)	119.3(4)
F(10)-C(24)-F(12)	108.4(6)	C(33)-C(38)-H(38)	120.3
F(10)-C(24)-F(11)	109.5(7)	C(37)-C(38)-H(38)	120.3
F(12)-C(24)-F(11)	100.8(5)	F(20)-C(39)-F(21)	108.4(5)
F(10)-C(24)-C(21)	113.3(5)	F(20)-C(39)-F(19)	104.2(5)
F(12)-C(24)-C(21)	111.2(5)	F(21)-C(39)-F(19)	106.1(4)
F(11)-C(24)-C(21)	112.8(4)	F(20)-C(39)-C(35)	112.5(4)
C(26)-C(25)-C(30)	121.4(4)	F(21)-C(39)-C(35)	114.2(5)
C(26)-C(25)-N(3)	120.7(4)	F(19)-C(39)-C(35)	110.8(5)
C(30)-C(25)-N(3)	117.7(3)	F(22)-C(40)-F(23)	109.6(4)
C(25)-C(26)-C(27)	117.9(4)	F(22)-C(40)-F(24)	107.1(5)
C(25)-C(26)-H(26)	121.1	F(23)-C(40)-F(24)	104.4(4)
C(27)-C(26)-H(26)	121.1	F(22)-C(40)-C(37)	112.5(4)
C(28)-C(27)-C(26)	122.2(4)	F(23)-C(40)-C(37)	110.5(4)
C(28)-C(27)-C(31)	119.5(4)	F(24)-C(40)-C(37)	112.3(4)
C(26)-C(27)-C(31)	118.3(4)	F(28)-B(1)-F(26)	113.2(4)
C(29)-C(28)-C(27)	118.4(4)	F(28)-B(1)-F(27)	109.7(4)
C(29)-C(28)-H(28)	120.8	F(26)-B(1)-F(27)	108.4(4)
C(27)-C(28)-H(28)	120.8	F(28)-B(1)-F(25)	109.1(4)
C(28)-C(29)-C(30)	121.2(4)	F(26)-B(1)-F(25)	108.3(4)
C(28)-C(29)-C(32)	120.0(4)	F(27)-B(1)-F(25)	108.0(4)
C(30)-C(29)-C(32)	118.7(4)	F(32)-B(2)-F(30)	114.0(4)
C(25)-C(30)-C(29)	118.9(4)	F(32)-B(2)-F(31)	112.8(4)
C(25)-C(30)-H(30)	120.5	F(30)-B(2)-F(31)	109.8(4)
C(29)-C(30)-H(30)	120.5	F(32)-B(2)-F(29)	108.8(4)
F(13)-C(31)-F(15)	106.5(4)	F(30)-B(2)-F(29)	105.1(4)
F(13)-C(31)-F(14)	105.4(4)	F(31)-B(2)-F(29)	105.7(4)

Table S10. Anisotropic displacement parameters ($Å^2 x 10^4$) for 5b (CCDC 204983).
The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	163(2)	127(1)	161(2)	11(1)	47(1)	2(1)
Pd(2)	140(1)	135(2)	156(1)	13(1)	42(1)	2(1)
F(1)	660(20)	650(20)	501(19)	-298(19)	71(16)	-130(20)
F(2)	1340(40)	720(30)	271(17)	47(18)	10(20)	-420(20)
F(3)	455(19)	970(30)	560(20)	-290(20)	27(16)	-280(20)
F(4)	750(20)	480(20)	1100(30)	290(20)	330(20)	418(19)
F(5)	269(16)	690(20)	620(20)	-76(17)	116(15)	114(15)
F(6)	334(17)	670(30)	780(20)	-423(19)	57(16)	128(15)
F(7)	1190(40)	2200(70)	1850(60)	-1590(60)	1160(40)	-730(40)
F(8)	4590(120)	1830(60)	1640(50)	1300(50)	2550(70)	2160(70)
F(9)	630(30)	2510(60)	960(30)	-530(40)	330(30)	580(40)
F(10)	4130(100)	1180(40)	540(30)	210(30)	-580(40)	-1860(60)
F(11)	520(20)	840(30)	710(20)	-440(20)	3(19)	20(20)
F(12)	460(20)	1560(40)	540(20)	-390(20)	-74(17)	110(20)
F(13)	700(20)	790(20)	501(18)	-50(20)	86(16)	-510(20)
F(14)	348(17)	940(30)	268(16)	-165(17)	88(14)	-143(18)
F(15)	465(19)	990(30)	430(18)	-236(19)	-201(15)	257(19)
F(16)	297(16)	770(20)	393(16)	-159(16)	59(13)	203(16)
F(17)	426(15)	309(15)	418(15)	-61(13)	184(12)	90(14)
F(18)	563(18)	496(19)	365(15)	53(14)	312(14)	99(15)
F(19)	442(19)	500(20)	1910(40)	140(30)	530(20)	185(19)
F(20)	410(20)	2050(50)	1140(30)	-1060(40)	340(20)	-30(30)
F(21)	409(17)	512(18)	1060(30)	-221(19)	463(18)	-84(16)
F(22)	550(20)	840(30)	600(20)	-450(20)	326(16)	-441(19)
F(23)	590(20)	600(20)	274(15)	-58(15)	153(14)	-97(16)
F(24)	710(20)	400(19)	590(20)	-166(15)	201(17)	-35(17)
O(1)	139(14)	200(15)	237(15)	39(12)	56(12)	-14(11)
O(2)	137(14)	191(15)	188(14)	81(12)	44(12)	20(11)
N(1)	176(18)	149(17)	181(17)	-47(14)	55(14)	-18(14)
N(2)	169(17)	153(17)	176(17)	10(14)	51(14)	33(14)
N(3)	148(16)	146(17)	145(16)	25(13)	57(13)	19(13)
N(4)	154(17)	169(17)	144(16)	25(13)	44(13)	27(13)
C(1)	260(20)	68(18)	240(20)	-28(16)	142(18)	-4(16)
C(2)	230(20)	110(19)	170(20)	-24(16)	66(17)	16(16)
C(3)	230(20)	190(20)	200(20)	9(18)	92(17)	7(18)
C(4)	220(20)	190(20)	220(20)	8(18)	93(17)	8(18)
C(5)	200(20)	230(20)	117(19)	-15(16)	75(17)	-24(17)
C(6)	230(20)	190(20)	108(19)	-19(15)	49(16)	30(17)
C(7)	230(20)	190(20)	250(20)	31(18)	68(19)	-20(18)
C(8)	310(30)	170(20)	240(20)	47(18)	40(20)	28(18)
C(9)	200(20)	146(19)	160(20)	14(16)	41(17)	-37(16)
C(10)	270(20)	240(20)	250(20)	-30(19)	100(20)	-77(19)
C(11)	360(30)	310(30)	250(30)	0(20)	30(20)	-140(20)
C(12)	230(20)	360(30)	290(20)	40(20)	-27(19)	-70(20)
C(13)	230(20)	180(20)	360(30)	7(19)	60(20)	5(18)
C(14)	240(20)	170(20)	196(19)	5(17)	36(16)	-29(17)
C(15)	290(30)	680(40)	310(30)	-20(30)	30(20)	-110(30)

C(16)	220(30)	370(30)	670(40)	-50(30)	50(30)	50(20)
C(17)	200(20)	160(20)	210(20)	93(17)	65(17)	32(16)
C(18)	200(20)	200(20)	200(20)	58(18)	56(18)	58(17)
C(19)	270(20)	280(20)	300(20)	170(20)	150(20)	120(20)
C(20)	170(20)	260(30)	360(30)	130(20)	30(19)	-23(19)
C(21)	250(20)	240(30)	320(20)	61(19)	6(19)	15(19)
C(22)	250(20)	160(20)	230(20)	60(19)	50(17)	40(19)
C(23)	350(30)	510(30)	290(30)	80(30)	140(20)	150(30)
C(24)	350(30)	550(40)	430(30)	-70(30)	40(30)	-150(30)
C(25)	170(20)	190(20)	190(20)	87(17)	93(17)	-15(17)
C(26)	230(20)	220(20)	220(20)	7(18)	100(18)	-39(18)
C(27)	180(20)	300(30)	240(20)	60(20)	75(19)	-7(19)
C(28)	160(20)	290(20)	290(20)	86(19)	82(19)	-17(18)
C(29)	230(20)	200(20)	270(20)	20(20)	124(17)	-30(20)
C(30)	170(20)	210(20)	180(20)	17(16)	62(16)	18(16)
C(31)	200(20)	460(30)	340(30)	-40(20)	50(20)	-50(20)
C(32)	210(20)	380(30)	300(30)	-10(20)	90(20)	40(20)
C(33)	190(20)	160(20)	140(20)	25(16)	0(16)	-12(17)
C(34)	240(20)	250(20)	230(20)	-72(18)	57(19)	28(19)
C(35)	230(20)	290(30)	380(30)	60(20)	110(20)	100(20)
C(36)	260(20)	330(30)	230(20)	20(20)	-21(18)	-50(20)
C(37)	280(20)	300(30)	220(20)	-32(18)	98(19)	-57(19)
C(38)	230(20)	260(20)	220(20)	-30(20)	95(16)	-10(20)
C(39)	180(30)	530(40)	810(50)	-200(30)	90(30)	10(20)
C(40)	280(30)	610(40)	280(30)	-110(20)	90(20)	-130(30)
B(1)	610(40)	160(30)	280(30)	20(20)	130(30)	0(30)
F(25)	490(18)	331(16)	409(17)	-64(13)	186(14)	-99(13)
F(26)	395(17)	309(15)	318(15)	-34(12)	34(13)	98(13)
F(27)	750(20)	209(15)	353(15)	86(11)	255(15)	18(13)
F(28)	700(20)	308(16)	310(16)	-40(13)	175(15)	44(15)
B(2)	410(30)	200(20)	220(30)	-60(20)	170(20)	-70(20)
F(29)	530(20)	490(20)	770(20)	92(18)	-131(18)	-62(16)
F(30)	1160(30)	244(15)	560(20)	-55(14)	630(20)	-23(17)
F(31)	531(15)	175(11)	245(12)	-37(13)	161(11)	4(13)
F(32)	598(17)	234(14)	247(13)	22(12)	181(12)	71(14)

Table S11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 5b (CCDC 204983).

	x	y	z	U_{iso}
H(3A)	3306	-1830	9963	30
H(3B)	4100	-1483	10844	30
H(3C)	4106	-2830	10355	30
H(4A)	6597	-2031	10872	31
H(4B)	5736	-2873	10839	31
H(4C)	5903	-1521	11349	31
H(7A)	6517	5501	6755	33
H(7B)	5743	6329	6952	33
H(7C)	5684	5990	5952	33
H(8A)	3251	5404	5613	37
H(8B)	4114	5909	5382	37
H(8C)	3968	6298	6303	37
H(10)	3133	-1774	7498	30
H(12)	748	-185	7318	38
H(14)	2904	548	9478	25
H(18)	6735	-1588	8517	24
H(20)	9137	-122	9927	33
H(22)	6994	421	10770	26
H(26)	7011	4162	8327	26
H(28)	9099	2298	7872	29
H(30)	6611	1992	6113	22
H(34)	2583	4191	6670	29
H(36)	772	1993	4843	36
H(38)	3408	1698	5124	28